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Microstructure Physics Group

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Research Activity

I. Syntheses and structural determination/characterization of micro- and mesoporous materials

1. Electron Crystallography for micro- and meso-porous crystals:

1-1. Three-dimensional structure of Mesoporous Materials,

(O. Terasaki, Y. Sakamoto, M. Kaneda, T. Tsubakiyama, T. Ohsuna, R. Ryoo, G. Stucky, & K. Hiraga)

Mesoporous silica materials have two structural characteristics, that is, disorder on the atomic scale (short-range) but distinct order on the mesoscopic scale (long-range). The self-organization of surfactants is a key mechanism for producing the periodic structure on the meso-scale, and both local and average structures of the organization is highly sensitive to synthesis conditions such as composition, temperature, and pH. From a very small crystal, we can, by EM, obtain single-crystal structural information, free from the local variations that typically contribute to both a small number of reflections and large peak widths in X-ray diffraction experiments. We have developed a new approach using electron crystallography to solve 3-D structures of mesoporous materials with disordered wall structures. The 3-D structural solution makes clear, at the nanoscale level, the size and shape of the pores and cages, their arrangements, and their connectivity, including sizes of openings.

1-2. Microporous crystals, zeolites.(T. Ohsuna, Z. Liu, K. Hiraga & O. Terasaki)

New framework-type structure of a zeolite was solved by information obtained only from transmision electron microscope. The framework structure was obtained from a few HRTEM images and some selected area electron diffraction(SAED) patterns. A new method for retrieving 3d-framework topology from a blurred potential-density map, which is Fourier reconstruction of HRTEM images, by Patterson map derived from SAED patterns, was applied to the determination.

2. Syntheses and structural characterization of novel porous crystals and clusters within the pores.

2-1. Formation of novel ordered mesoporous silicas with square channels and the direct TEM observation (M. Kaneda, Y. Sakamoto, O. Terasaki & K. Kuroda)

All the structures of mesoporous silicas reported so far have been governed primarily by the geometrical packing of surfactants. We study the formation of novel mesoporous silicas (denoted as KSW-2) with square or lozenge one-dimensional (1-D) channels, which have never been found among previously reported organizations of surfactants and hence among mesoporous silicas, by mild acid-treatment of a layered alkyltrimethylammonium (C_nTMA)–kanemite complex.

2-2. Syntheses of novel microporous crystals(J. Yu, G. Zhu, S. Qiu, & O. Terasaki)

(a) Assembly of One-Dimensional $AlP_2O_8^{3-}$ Chains through Ni Octahedra.

(b) An Anionic Aluminophosphate Molecular Sieve.

(c) The synthesis of offretite single crystals

2-3. TEM Studies of Platinum Nanowires Fabricated in Mesoporous Silicas MCM-41 and MCM-48. (Z. Liu, Y. Sakamoto, T. Ohsuna, K. Hiraga, O. Terasaki & R. Ryoo).

Pt-nanowires were synthesized within the pores/channels of MCM-41 and MCM-48, and their structures were characterized by high-resolution transmission electron microscopy and X-ray powder diffraction. We could show mesoporous silicas can be used as templates for making new materials. Single-crystal Pt-nanowires with a pore diameter of ca. 30 Å, pore size of MCM-41, were synthesized. <110> axes are the preferential growth directions of the Pt nanowires. A three-dimensional chiral network of Pt-nanowires 3-nm in diameter was synthesized using MCM-48 silica as template. The Pt-nanowires have new hierarchy ordered structures in two length scales, on atomic and mesoscopic scales, with the cubic $P4_132$ and cubic $P4_332$ SG symmetries corresponding to the two independent channel systems in MCM-48.

II. Alkali Metal Clusters in Zeolite Cages

1. Ferromagnetic properties of rubidium clusters in zeolite LTA (T. Nakano, Y. Ikemoto and Y. Nozue, published in J. Mag. Mag. Mat. **226-230** (2001) 238-240.)

Magnetic and optical properties are investigated in detail for Rb clusters arrayed in a simple cubic structure in zeolite LTA. The average number of *s*-electrons confined in each cluster, n, is changed up to the nearly saturated value ~ 4.6. At $n > 2$, the absolute value of the negative Weiss temperature increases with increasing n. In saturated samples at n ~ 4.6, ferromagnetic properties are observed below the asymptotic Curie temperature 3 K, but the fraction of the spontaneous magnetization is found to be very small. Magnetic properties are different from those of K clusters in LTA. The ferromagnetic properties are discussed in relation to residual K cations.

2. Electron spin resonance study and orbital degeneracy of potassium clusters in zeolite LTA (T. Nakano, Y. Ikemoto and Y. Nozue)

K clusters can be arrayed in a simple cubic structure by the loading of K metal into the α cages of aluminosilicate zeolite LTA, where the α cage has an inside diameter of ~ 11 Å. The average number of 4*s* electrons per α cage, *n*, can be controlled up to ~ 7.2 by adjusting the loading density of K atoms. The 4*s* electrons successively occupy the 1*s*- and 1*p*-like quantum electronic states of K cluster, i.e. first two for 1*s*- and next six for 1*p*-state. At $n > 2$, where the 4*s* electrons occupy the 1*p*-state, the g value is found to decrease suddenly. For ferromagnetic samples at $2 < n < 6$, the g value obviously decreases at low temperature. Usually, the decrease in *g* value originates from the spin-orbit interaction. The orbital degeneracy of 1*p*-state is thought to enhance the spin-orbit interaction at low temperature in the ferromagnetic samples. Generally, it is known that the orbital degeneracy remarkably enhances the DM interaction. In conclusion, the orbital degeneracy of 1*p*-state is responsible for the spontaneous magnetization.

3. Insulating phase of potassium clusters arrayed in low-silica type zeolite FAU (Y. Ikemoto, T. Nakano, M. Kuno, Y. Nozue and T. Ikeda, published in J. Mag. Mag. Mat. **226-230** (2001) 229-232.)

Mutually interacting potassium clusters stabilized in supercages of aluminosilicate zeolite FAU (Si/Al = 1), so-called the low-silica X, are investigated in terms of optical and magnetic properties. FAU is ion-exchanged to K, and denoted by K-FAU(1), hereafter. When K metal is adsorbed at the average loading density of 0.7 ± 0.3 atom per supercage of FAU, the observed infrared absorption is more than one order weaker than that in similarly K-loaded samples of K-FAU(1.25) which is called X commonly. The Weiss temperature in K-loaded K-FAU(1) is –33 ± 3 K. This value is several times larger than that in K-loaded K-FAU(1.25). The Mott insulator phase is thought to be realized in K clusters in FAU(1), differently from the metallic phase of K-FAU(1.25).

Master Theses

M1) Structural study of carbon-networks synthesized within the pores of silica mesoporous MCM-48 by Electron Microscopy, Toshikazu Tsubakiyama

M2) Microoptical study of silicon clathrate compounds, Gentaro Hosaka

Doctor Thesis

D1) Magnetic and optical properties of alkali metal clusters incorporated in zeolite LTA, Takehito Nakano

Publications

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13. Size-controlled synthesis of silicalite-1 single crystals in the presence of benzene-1,2-diol, C. Shao, X. Li, S. Qiu, F-S. Xiao & O. Terasaki, *Microporous and Mesoporous Materials*, **39** (2000), 117-123.

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